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A reexamination of the turquoise group: the mineral aheylite, planerite (redefined), turquoise and coeruleolactite

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ABSTRACT

The turquoise group has the general formula: $A_{0-1}B_6(PO_4)_{4-x}(PO_3OH)_x(OH)_8{\cdot}4H_2O$, where x = 0–2, and consists of six members: planerite, turquoise, faustite, aheylite, chalcosiderite and an unnamed Fe^{2+}–Fe^{3+} analogue. The existence of 'coeruleolactite' is doubtful. Planerite is revalidated as a species and is characterized by a dominant A-site vacancy. Aheylite is established as a new member of the group, and is characterized by having Fe^{2+} dominant in the A-site.

Chemical analyses of 15 pure samples of microcrystalline planerite, turquoise, and aheylite show that a maximum of two of the (PO_4) groups are protonated (PO_3OH) in planerite. Complete solid solution exists between planerite and turquoise. Other members of the group show variable A-site vacancy as well. Most samples of 'turquoise' are cation-deficient or are planerite. Direct determination of water indicates that there are 4 molecules of water.

Planerite, ideally $\square Al_6(PO_4)_2(PO_3OH)_2(OH)_8{\cdot}4H_2O$, is white, pale blue or pale green, and occurs as mamillary, botryoidal crusts as much as several mm thick; may also be massive; microcrystalline, crystals typically 2–4 micrometres, luster chalky to earthy, H. 5, somewhat brittle, no cleavage observed, splintery fracture, D_m 2.68(2), D_c 2.71, not magnetic, not fluorescent, mean RI about 1.60. a 7.505(2), b 9.723(3), c 7.814(2) Å, α 111.43°, β 115.56°, γ 68.69°, V 464.2(1) $Å^3$, Z = 1.

Aheylite, ideally $Fe^{2+}Al_6(PO_4)_4(OH)_8{\cdot}4H_2O$, is pale blue or green, and occurs as isolated and aggregate clumps of hemispherical or spherical, radiating to interlocked masses of crystals that average 3 micrometres in maximum dimension; porcelaneous-subvitreous luster, moderate to brittle tenacity, no cleavage observed, hackly to splintery fracture, not magnetic, not fluorescent, biax. (+), mean RI is about 1.63, D_m 2.84(2), D_c 2.90. a 7.400(1), b 9.896(1), c 7.627(1) Å, α 110.87°, β 115.00°, γ 69.96°, V 460.62(9) $Å^3$, Z = 1.

KEYWORDS: turquoise group, planerite, aheylite, 'coeruleolactite', X-ray diffraction data.

Introduction

MINERALS of the turquoise group have been known since antiquity and have been valued for their use as gems. Pogue (1915) summarized what was known about turquoise in his monograph. However, the structure and chemistry of members of the group (Table 1) were not clear until relatively recently (Cid-Dresner, 1964, 1965; Cid-Dresner and Villarroel, 1972; and Guthrie and Bish, 1991, for turquoise; Giuseppeti *et al.*, 1989, for chalcosiderite; Foord and Taggart, 1986, for planerite and aheylite). This paper presents new complete chemical analyses of 15 pure samples and summarizes the elemental site occupancies of the various sites for the members

TABLE 1. Members of the turquoise group: general-formula: $A_{0-1}B_6(PO_4)_{4-x}(PO_3OH)_x(OH)_6{\cdot}4H_2O$ where $x = 0-2$

A-site	*B*-site	$(PO_4)_{4-x}$	$(PO_3OH)_x$	Mineral name
□	Al	2	2	Planerite
Cu	Al	4	0	Turquoise
Zn	Al	4	0	Faustite
Fe^{2+}	Al	4	0	Aheylite
Ca?	Al	4	0	Coeruleolactite
□	Fe^{3+}	2	2	unknown as yet
Cu	Fe^{3+}	4	0	Chalcosiderite
Zn	Fe^{3+}	4	0	unknown as yet
Fe^{2+}	Fe^{3+}	4	0	(unnamed)*
Ca?	Fe^{3+}	4	0	unknown as yet

* First reported by Mücke (1981) from Hagendorf, but without supporting chemical and structural data. Mücke (personal communication (1983) provided the authors with full data for the mineral, as submitted to the CNMMN IMA. The mineral was approved, but the proposed name was not.

of the turquoise group. It also presents results of an examination of two specimens of blue to blue-green 'coeruleolactite' from the type locality.

Turquoise and other members of the group do not contain 5 molecules of water as has been shown by some authors to the present time, but only 4 molecules. The crystal structure determinations (Cid-Dresdner, 1964, 1965; Giuseppeti, *et al.*, 1989; Guthrie and Bish, 1991) for turquoise and chalcosiderite also indicate four molecules to be present. As vacancy becomes dominant in the *A*-site, then the amount of protonation, to a maximum of two of the phosphate groups, increases. Charge balance is maintained by the development of (PO_3OH) groups as the *A*-site occupancy decreases. The two sites for H are what principally caused the number of molecules of molecular water to previously be reported as 4 or 5. Some minor H_2O for OH substitution may also occur. Alteration processes such as those described by Van Wambeke (1971) do not account for the *A*-site cation deficiency in turquoise group minerals.

A chemical, X-ray and Mössbauer examination of a turquoise from Greece (Sklavounos *et al.*, 1992) showed 9.09 wt.% CuO, 0.26 wt.% BaO, Al_2O_3 35.7, Fe_2O_3 1.27, As_2O_5 0.14, P_2O_5 34.00 and 19.41 wt.% H_2O (by difference). This is clearly a high Cu-containing turquoise with essentially no *A*-site vacancy. The 19.41 wt.% H_2O, assigned by difference, is substantially more than the ideal amount of 17.72 wt.% H_2O. P_2O_5 is about 1 wt.% low from that for theoretical turquoise. It is unfortunate that a direct determination for water was not done.

In the case of the 'cuprofaustite' described by Kunov *et al.* (1982), this mineral is clearly a cation-deficient (*A*-site deficient) faustite. The turquoise from the Kelly Bank mine, Rockbridge Co., VA (Mitchell and Freeland, 1978; Barwood and Zelazny, 1982) has been shown to be planerite (this study). The mineral described by Ivanov (1979) is best described as a cation-deficient aluminian chalcosiderite. Similarly, the turquoise described from Paikhoy, Russia (Belyaev and Ievlev, 1990) is best characterized as a Cu-Fe bearing planerite. The turquoises (microprobe analyses with no direct determination of water) described by Silaev *et al.* (1995) from Paikhoy and other locations in the Ural Mountains are turquoise-planerite.

Analytical methods

Cations (Cu,Zn,Fe,Al,P) were determined on small, hand picked samples ranging from 4 to 12 mg using the ICP technique described in Lichte *et al.* (1983, 1987). Early in this work samples were digested with KOH fusion at 500°C. Later in this technique the digestion was improved and 1 mg of sample was digested per ml of high purity 6 N HCl (prepared by gaseous transfer of HCl from concentrated hydrochloric acid over to double distilled water) using small volumetric tubes, a stirring hot plate at 80° C, and a micro-magnetic stir bar.

H_2O^- was determined gravimetrically after drying at 105°C for four days. After drying, the sample was then analysed for water at 900°C by Karl Fisher titration using the technique of Jackson *et al.* (1985, 1987) and the results were then reported as H_2O^+

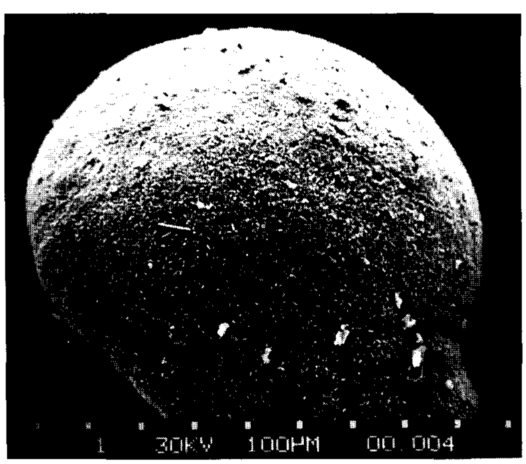
Samples examined

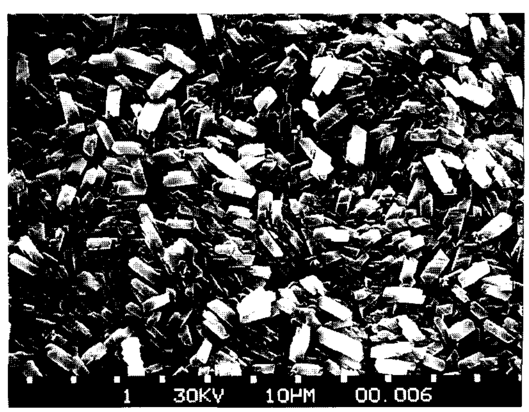
Analyses for a total of 15 samples of planerite, aheylite, and turquoise, many with their museum catalogue numbers, ideal compositions for turquoise, planerite and aheylite, along with one unpublished analysis of planerite from Arkansas, are given in Table 2. Every effort was made to obtain early specimens of 'type' planerite from the Gumeshevsk copper mine, Urals, Russia, so that the mineral could be properly revalidated. True type samples were not preserved as such in the mid-19th century. One specimen of planerite was obtained from The Natural History Museum, London (specimen no. BM 36020, acquired about 1864), along with one specimen (dated 1869) from Harvard University (specimen 62121, Liebener collection). Two old specimens were obtained from the USNM (nos. R5524 and R9710). Additional specimens of planerite were obtained from Charles University (Prague) (12389), and (unnumbered) from the Mining Institute of Leningrad (Gorny Institute). Specimens of planerite were also obtained from the Bryn Mawr College collection (Rand Collection #8520). We also obtained some turqoise (USNM # 97340) from the Bishop mine, Lynch Station, VA that had been studied by Schaller (1912). Five samples of aheylite were provided by Mr Richard A. Kosnar, and one by Mr Anthony Jones. Many attempts were made to find, for analysis, specimens of white and blue varieties of 'coeruleolactite' from the Rindsberg mine, Katzenelnbogen (also spelled Katzenellenbogen), Hesse (formerly Nassau), Germany, but only two specimens (of the blue to blue-green variety) were able to be obtained through the courtesy of Mr Forrest Cureton (one specimen), and H.J. and I.A. Wilke (given to Mr David Garske who gave the second specimen to Mr Forrest Cureton).

SEM-EDS studies

A Cambridge Stereoscan 250 Mk-1 instrument with attached Tracor Northern EDS system was used for examination, chemical characterization, and photomicrographs of all turquoise group minerals examined.

Most specimens of members of the turquoise group are microcrystalline and apppear as earthy, fine-grained, variable density materials. However, the specimens of aheylite and planerite examined in this study along with some turquoise samples are micro-crystalline to macrocrystalline. SEM photos (Figs 1–8) show the complex and excellent crystallinity of these minerals. It





FIGS 1 and 2. FIG. 1 (*left*). SEM photo of a sphere of aheylite crystals from Huanuni, Bolivia. FIG. 2 (*right*). SEM photo at intermediate power showing diamond-shaped crystals making up the sphere shown in Fig. 1.

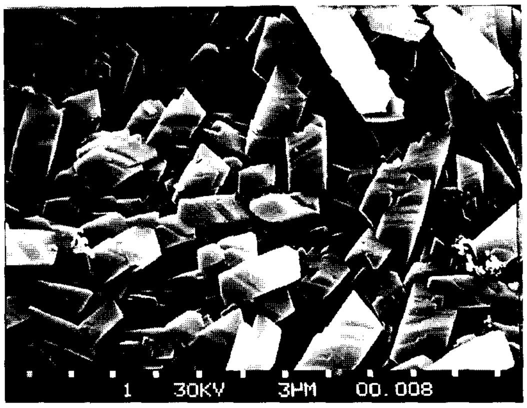
TABLE 2. Chemical analyses of members of the turquoise group including the unpublished analysis by M.D. Foster of planerite from Arkansas

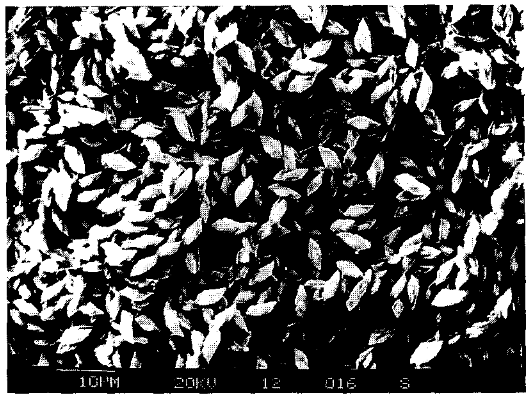
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
CuO	–	–	–	–	–	–	–	–	3.92	3.93	9.78	9.00	8.81	3.41	2.33	3.10	0.99	0.40	0.23	–	3.08	–
ZnO	3.39	4.48	4.18	–	4.02	2.52	1.54	–	0.66	0.91	–	–	0.14	0.19	0.14	0.74	0.15	0.07	0.03	–	–	–
FeO	4.14	4.23	4.06	–	4.14	4.91	3.22	8.92	–	–	–	–	–	–	–	–	–	–	–	–	0.23	–
Fe_2O_3	–	–	–	–	–	–	–	–	–	–	–	0.21	0.28	0.49	0.87	0.46	0.44	0.21	0.00	0.8	0.86	–
Al_2O_3	39.5	38.0	36.9	–	38.1	38.1	38.9	37.96	38.2	37.5	37.60	36.50	37.7	38.2	–	–	–	39.9	39.5	40.1	37.75	40.68
P_2O_5	34.3	36.0	35.8	–	35.4	36.1	36.7	35.23	36.4	35.9	34.90	34.13	34.5	36.3	–	–	–	38.2	37.3	37.1	35.75	37.76
H_2O^+	–	–	–	18.5	18.5	18.4	19.5	17.89	19.0	19.0*	17.72	–	18.2	19.7	19.5	17.7	19.4	21.0	20.8	20.4	21.21	21.56
H_2O_{total}	–	–	–	18.6	–	–	–	–	–	–	–	20.12	–	–	–	–	–	–	–	21.1	–	–
H_2O^-	–	–	–	0.08	0.08	0.10	1.20	0.00	3.27	3.27	0.00	–	0.45	1.60	–	–	–	0.84	1.23	0.87	.12	0.00
Total	–	–	–	–	100.24	100.13	101.06	100.00	101.45	100.51	100.00	99.96	100.08	99.89		–	–	100.62	99.09	99.27	100.10	100.00

TABLE 2 (*contd.*)

1. Aheylite, Huanuni Mine, District of Oruro, Bolivia, ICP analysis of KOH fusion at 500° C, 8.08 mg. Sample from R.A. Kosnar.
2. Aheylite, Huanuni Mine, District of Oruro, Bolivia, ICP analysis of KOH fusion at 500° C, 8.84 mg. Sample from R.A. Kosnar.
3. Aheylite, Huanuni Mine, District of Oruro, Bolivia, ICP analysis of KOH fusion at 500° C, 9.96 mg. Sample from R.A. Kosnar.
4. Aheylite, Huanuni Mine, District of Oruro, Bolivia, H_2O^- gravimetrically, H_2O+ by Karl Fisher titration. Sample from R.A. Kosnar.
5. Aheylite, Huanuni Mine, District of Oruro, Bolivia, average of 1, 2, 3, and 4. Samples from R. A. Kosnar.
   $(FeZn_{0.40}\square_{0.14})Al_6(PO_4)_{3.72}(PO_3OH)_{0.28}(OH)_8 \cdot 4.10\ H_2O$
6. Aheylite, Huanuni Mine, District of Oruro, Bolivia, ICP analysis 7.49 mg sample. H_2O^- gravimetrically, H_2O^+ by Karl Fisher titration, 8.59 mg sample. Samples from A. Jones, Duarte, California.
   $(FeZn_{0.25}\square_{0.20})Al_6(PO_4)_{3.68}(PO_3OH)_{0.40}(OH)_8 \cdot 4.00\ H_2O$
7. 'Half empty' aheylite-planerite, Huanuni Mine, District of Oruro, Bolivia, ICP analysis 4.76 mg sample. H_2O^- gravimetrically, and H_2O^+ by Karl Fischer titration, 5.828 mg sample.
   $(\square_{0.50}\ Fe_{35}Zn_{0.15})Al_6(PO_4)_{3.07}(PO_3OH)_{1.00}(OH)_8 \cdot 4.01\ H_2O$
8. Ideal aheylite.
   $Fe^{2+}Al_6(PO_4)_4(OH)_8{\cdot}4\ H_2O$
9. "Half empty" planerite-turquoise, General Trimble's Mine, Pennsylvania, Bryn Mawr College, Rand collection #8520, ICP analysis 10.39 mg sample. H_2O^- gravimetrically, H_2O^+ by Karl Fisher titration, 10.4 mg sample.
   $(\square_{0.54}Cu_{0.40}Zn_{0.06})Al_6(PO_4)_{3.03}(PO_3OH)_{1.08}(OH)_8{\cdot}3.91\ H_2O$
10. 'Half empty' planerite-turquoise, General Trimble's Mine, Penn., Bryn Mawr College, Rand collection #8520, ICP analysis 7.57 mg sample. *Water from determination reported in analysis #9.
   $(\square_{0.51}Cu_{0.40}Zn_{0.09})Al_6(PO_4)_{3.11}(PO_3OH)_{1.02}(OH)_8{\cdot}4.09\ H_2O$
11. Ideal turquoise.
   $Cu\ Al_6(PO_4)_4(OH)_8{\cdot}4\ H_2O$
12. Turquoise, Lynch Station, Virginia. Analysis by Schaller (1912) American Journal of Science, 33, p. 35. Schaller performed a Penfield analysis for total water.
   $(Cu_{0.95}\ \square_{0.05})(Al_{5.98}Fe_{0.02})(PO_4)_{3.91}(PO_3OH)_{0.10}(OH)_8{\cdot}5.27\ H_2O$
13. Turquoise, Lynch Station, Virginia. New analysis of Schaller's U.S.N.M. 97340 sample. ICP analysis of 5.617 mg. Iron determined as total iron and expressed as Fe_2O_3. H_2O^- gravimetrically, H_2O^+ by Karl Fisher titration, 5.780 mg sample. 1.86% insoluble residue (quartz) 'normalized out.'
   $(Cu_{0.89}\ \square_{0.10}Zn_{0.01})(Al_{5.97}Fe_{0.03})(PO_4)_{3.73}(PO_3OH)_{0.20}(OH)_8{\cdot}4.06\ H_2O$
14. Planerite, Mt. Tschernov, Gumeshevsk, Urals, U.S.S.R. Harvard #62121, L. Liebener Collection (1869) ICP analysis of 11.877 mg sample. H_2O^- gravimetrically, H_2O^+ by Karl Fisher titration, 13.055 mg sample.
   $(\square_{0.64}\ Cu_{0.34}\ Zn_{0.02})(Al_{5.95}Fe_{0.05})(PO_4)_{2.78}(PO_3OH)_{1.28}(OH)_8{\cdot}4.04\ H_2O$
15. Planerite Gumeshevsk, Urals, U.S.S.R., sample from D.P.Gregoryev, Mining Institute of Leningrad. ICP analysis of 4.773 mg sample. Separate sample dried at 105°C, then H_2O^+ by Karl Fisher titration.
16. Planerite, Urals, U.S.S.R. British Museum BM 36020 entered into the collection in 1864. ICP analysis of 6.090 mg sample. Separate sample dried at 105°C, then H_2O^+ by Karl Fischer titration.
17. Planerite, Urals, U.S.S.R. Charles University, Prague, Czechoslovakia, #12389. ICP analysis of 5.355 mg sample. Separate sample dried at 105°C, then H_2O^+ by Karl Fischer titration.
18. Planerite, Syssert District, Urals, U.S.S.R., U.S.N.M. R5524. Average of duplicate ICP analyses of 8.876 and 9.283 mg samples. H_2O^- gravimetrically, H_2O^+ by Karl Fisher titration, 5.376 mg sample.
   $(\square_{0.95}\ Cu_{0.04}\ Zn_{0.01})(Al_{5.98}Fe_{0.02})(PO_4)_{2.21}(PO_3OH)_{1.90}(OH)_8{\cdot}3.96\ H_2O$
19. Planerite, Gumeshevsk, Urals, U.S.S.R., U.S.N.M. R9710. ICP analysis of 10.544 mg sample. H_2O^- gravimetrically, H_2O^+ by Karl Fisher titration, 14.892 mg sample.
   $(\square_{0.98}\ Cu_{0.02}\ Zn_{0.003})Al_6(PO_4)_{2.11}(PO_3OH)_{1.96}(OH)_8{\cdot}3.96\ H_2O$
20. Planerite, Mauldin Mountain quarry, Mt. Ida, Montgomery Co. Arkansas. Microprobe analysis and total water (Penfield) by P.J. Dunn. H_2O^- gravimetrically, H_2O^+ by Karl Fisher titration.
   $\square_{1.00}(Al_{5.92}Fe_{0.08})(PO_4)_{1.92}(PO_3OH)_{2.00}(OH)_8{\cdot}4.07\ H_2O$
21. Planerite-turquoise, Dug Hill, Arkansas, collected by W.T.Schaller in 1937, analysis by Margaret Foster , August 29, 1951, using classical methods. TiO_2 0.67%, Cr_2O_3 0.19%, V_2O_5 0.20%, K_2O 0.03%, Na_2O 0.01
   $(\square_{0.67}\ Cu_{0.31}\ Fe_2\ )(Al_{5.89}Fe_{0.09}Cr_{0.02})(PO_4)_{2.72}(PO_3OH)_{1.29}(OH)_8{\cdot}4.73\ H_2O$
22. Ideal planerite.
   $\square_{1.00}Al_6(PO_4)_2(PO_3OH)_2(OH)_8{\cdot}4\ H_2O$

Note: Structural formulas calculated on the basis of the following assumptions: B site occupancy (Al, Fe^{3+}, Cr) equaling 6.0; H was distributed in the following sequence: H_2O^- was not used, H_2O^+ was distributed to $(OH)_8$ based on assumed stoichiometry; the number of PO_3OH molecules was determined by calculating charge balance, and the remainder of the H placed in the molecular water site $({\cdot}H_2O)$.



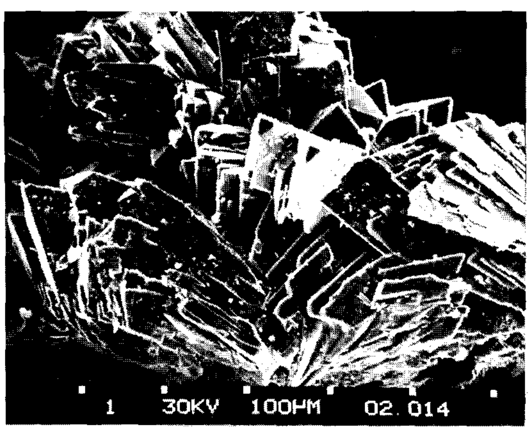


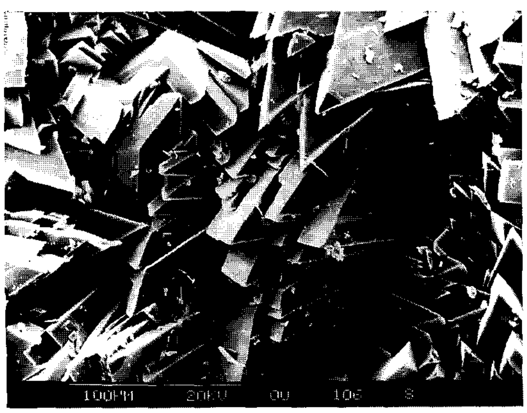
FIGS 3 and 4. FIG. 3 (*left*). SEM photo at high power showing individual crystals of aheylite shown in Figs 2 and 3. FIG. 4 (*right*). SEM photo of planerite crystals (R9710) from Gumeshevsk, Urals, Russia.

should be pointed out that many crystalline samples of turquoise group members are chemically zoned and this chemical zonation often correlates with colour zonation of various samples. For example darker green zones contain more iron, darker blue zones contain more copper, and rarely other elements such as Cr, V, and Zn show up as well.

TGA and Mössbauer data

TGA studies were done in the laboratory of C. Gene Whitney (USGS). Both his assistance and that of Kenneth J. Esposito, enabled us to do this important aspect of characterization of the members of the turquoise group. Instrumentation used was a Perkin-Elmer TGA 300 system. Mössbauer data were collected through the courtesy of D.L. Williamson (Colo. School of Mines). TGA data for two planerites (R9710 and R5524) indicate three discrete weight loss events: 1. 170–200°C (H_2O), 2. 280–300°C (OH) and 3. 340°C (PO_3OH) (Fig. 9). Turquoise from Lynch Station, VA (9% vacancy) shows only one weight loss event at 420°C (Fig. 10). Similar results for Lynch Station turquoise were obtained by Mr. Henry Barwood (Indiana Geological Survey). The molecular water in fully or nearly completely *A*-site filled turquoise is tightly bound and is released together with (OH). To check the





FIGS 5 and 6. FIG. 5 (*left*). SEM photo of Lynch Station, VA, turquoise crystals (USNM #97340). FIG. 6 (*right*). SEM photo of turquoise crystals from Itatiaiucu iron mine, Minas Gerais, Brazil.